

OPI DATE 11/08/97 APPLN. ID 15742/97  
AOJP DATE 02/10/97 PCT NUMBER PCT/US97/00309



AU9715742

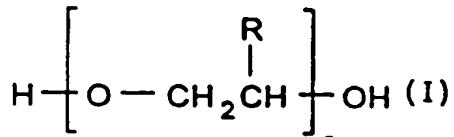
INTEI

(S1) International Patent Classification 6 :	A1	(11) International Publication Number: WO 97/25963
A61K 7/06		(43) International Publication Date: 24 July 1997 (24.07.97)
(21) International Application Number: PCT/US97/00309		(81) Designated States: AU, BR, CA, CN, JP, KR, MX, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).
(22) International Filing Date: 10 January 1997 (10.01.97)		
(30) Priority Data: 08/586,435 16 January 1996 (16.01.96) US		Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(71) Applicant: THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).		
(72) Inventors: RANEY, David, Jr.; 8949 B. Harperpoint Drive, Cincinnati, OH 45249 (US). HOPKINS, Jeffrey, Jon; 7856 Tylers Way, West Chester, OH 45069 (US). DODD, Michael, Thomas; 1210 Bobwhite, Edgewood, KY 41018 (US). FEATHERSTON, John, Paul; 586 Empress Avenue, Cincinnati, OH 45226 (US).		
(74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		

(54) Title: HAIR CONDITIONING COMPOSITIONS

(57) Abstract

Provided are leave-on hair care compositions which can impart enhanced hair conditioning and damage protection, while being formulated in a low viscosity product. In particular, the atomizable leave-on hair care composition comprise: (i) from about 0.1 % to about 10 %, by weight, of a cationic cross-linked polymeric conditioning agent comprising the monomer units  $(A)_m(B)_n(C)_p$  and a cross-linking agent wherein: (A) is a dialkylaminoalkyl acrylate monomer or a quaternary ammonium or acid addition salt thereof; (B) is a dialkylaminoalkyl methacrylate monomer or a quaternary ammonium or acid addition salt thereof; (C) is a nonionic monomer polymerized with (A) or (B); m, n and p are independently zero or greater, but at least one of m or n is one or greater; (ii) from about 0.1 % to about 10 %, by weight, of a salt; and (iii) from about 0.0001 % to about 0.05 % of at least one polyalkylene glycol corresponding to the structure (I), wherein R is H or  $\text{CH}_3$  and r is an integer from about 2000 to about 25,000; (d) from about 60 % to about 99.7999 %, by weight, of a polar solvent; wherein the weight ratio of said cationic cross-linked polymeric conditioning agent to said salt is from about 1:25 to about 25:1; and wherein the viscosity of the composition is from about 10 cP to about 500 cP as measured using a Brookfield Viscometer, Spindel #41, at 25 °C, at 10 RPM for three minutes.



## HAIR CONDITIONING COMPOSITIONS

5

TECHNICAL FIELD

The present invention relates to atomizable non-aerosol leave-on hair  
10 care compositions which provide improved hair conditioning properties. These compositions comprise a cationic crosslinked polymeric conditioning agent, a salt, a high molecular weight polyethylene glycol and a polar solvent. These products have an unexpected low viscosity compared to traditional products containing said conditioning agents.

15 BACKGROUND OF THE INVENTION

Non-aerosol sprays are a popular form for conveniently delivering a wide variety of hair care products. However, a common problem with many non-aerosol sprays is that they tend to deliver streams or dribbles of product rather than a uniformly atomized spray. Even those products which appear  
20 to be fully atomized are often found, upon closer examination, to possess "hot spots", i.e. areas of incompletely atomized product, or do not provide a solid pattern. Uniform delivery of a spray product is an important benefit, especially for products applied to the hair, to avoid overspraying during application.

25 Hair care spray products of the prior art also suffer from the disadvantage of not affording users with an adequate degree of application control. These products dispense with a wide cone angle, causing the product to drift or be unintentionally sprayed onto surfaces to which application of the product is not intended. Additionally, this lack of  
30 application control results in product wastage.

Another disadvantage of many of the hair care spray products of the prior art is that the pump dispensers are difficult to operate, requiring an inconveniently large amount of force and number of strokes to prime the pump to properly dispense the product as a spray.

35 Additionally, many of the spray products of the past relied almost exclusively upon aerosol containers to deliver fine, uniform spray mists. With the concern for the effects of fluorocarbons on the ozone layer and the

advent of restrictions against the use of fluorocarbons in atomizing dispensers, the development of compositions which can be delivered by non-aerosol spray containers has become increasingly important.

Crosslinked polymeric conditioning agents have been disclosed in the art as conditioning agents, thickening agents or hair damage prevention agents. PCT Application WO 94/10833 to Cox, et al. published April 13, 1995 discloses hair care compositions containing crosslinked polymeric conditioning agents in compositions, for improved hair shine benefits. These conditioning agents, although effective, have a viscosity building effect and are most suitable for cream and lotion shampoos and conditioners. However, the resulting high viscosities of hair care compositions containing these crosslinked polymeric conditioning agents have prevented the use of these agents in low viscosity products such as non-aerosol sprays.

Therefore, it would be highly desirable to develop non-aerosol products containing crosslinked polymeric conditioning agents which overcome the disadvantages of the prior art.

It is therefore an object of the present invention to provide atomizable hair spray products which possess superior delivery and atomization characteristics when delivered from a spray pump. Another object of the present invention is to deliver fine, uniform spray mists which do not stream and dribble and which a solid pattern of atomized product. It is another object of the present invention to provide spray products which when used in pump dispensers are easy to dispense. It is a further object of the present invention to deliver improved spray products without resorting to less desirable aerosol sprays. It is a still further object of the present invention to provide methods for providing improved delivery of an atomizable hair care composition.

These and other objects and benefits of the present invention as may be set forth herein as may now or later become apparent to those skilled in the art can be provided according to the invention which is described herein.

The invention hereof can comprise, consist of, or consist essentially of the essential elements described herein as well as any of the preferred or other optional ingredients described herein.

All percentages herein are by weight of the total composition unless otherwise indicated. All ratios are weight ratios unless otherwise indicated. Unless otherwise indicated, all percentages, ratios, and levels of ingredients

referred to herein are based on the actual amount of the ingredient, and do not include solvents, fillers, or other materials with which the ingredient may be combined in commercially available products. All measurements are at 25°C or room temperature, unless otherwise designated.

5 All documents referred to herein, including all patents, all patent applications, all articles, all bulletins, all pamphlets, and all technical data sheets are incorporated herein by reference in their entirety.

#### SUMMARY OF THE INVENTION

The present invention relates to leave-on hair care compositions that  
10 can provide enhanced hair conditioning and damage prevention, while being formulated in a low viscosity product for ease of application after bathing or showering. In particular, the present invention relates to leave-on hair care compositions comprising:

An atomizable leave-on hair care composition comprising:

15 (i) from about 0.1% to about 10%, by weight, of a cationic crosslinked polymeric conditioning agent comprising the monomer units (A)<sub>m</sub> (B)<sub>n</sub> (C)<sub>p</sub> and a crosslinking agent wherein:

(A) is a dialkylaminoalkyl acrylate monomer or a quaternary ammonium or acid addition salt thereof;

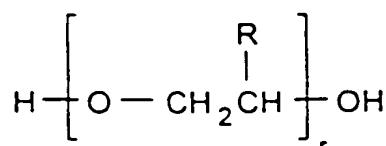
20 (B) is a dialkylaminoalkyl methacrylate monomer or a quaternary ammonium or acid addition salt thereof;

(C) is a nonionic monomer polymerizable with (A) or (B);

m, n, and p are independently zero or greater, but at least one of m or n is one or greater;

25 (ii) from about 0.1% to about 10%, by weight, of a salt; and

(iii). from about 0.0001% to about 0.05% of at least one polyalkylene glycol corresponding to the structure



30 wherein R is H or CH<sub>3</sub> and r is an integer from about 2000 to about 25,000;

(d) from about 60% to about 99.7999%, by weight, of a polar solvent;

35 wherein the weight ratio of said cationic crosslinked polymeric conditioning agent to said salt is from about 1:25 to about 25:1; wherein the viscosity of

the composition is from about 10 cP to about 500 cP as measured using a Brookfield Viscometer, Spindel #41, at 25°C. at 10 RPM for three minutes.

The present invention also relates to methods for conditioning human hair comprising the application of a safe and effective amount of the hair care composition described above to the hair of a human in need of such treatment.

#### DETAILED DESCRIPTION OF THE INVENTION

The term "leave-on", as expressed herein to modify the term "hair care composition", is used to indicate that the compositions of the present invention are intended to be applied to and allowed to remain on the hair. These leave-on compositions are to be distinguished from "rinse-off" compositions which are applied to the hair and subsequently removed, either immediately or after a few minutes, either by washing, rinsing, wiping or the like.

The essential ingredients as well as a variety, but non-exclusive, list of preferred and optional ingredients are described below.

#### Cationic Crosslinked Polymeric Conditioning Agent

The compositions of the present invention comprise from about 0.1% to about 10%, more preferably from about 0.2% to about 5%, and most preferably from about 0.5% to about 3% of a cationic crosslinked polymer conditioning agent. The cationic crosslinked polymers hereof provide improved hair conditioning and damage prevention benefits upon application to the hair.

Crosslinked polymers of the type for use herein are generally described in U.S. Patent 5,100,660, to Hawe et al., issued March 31, 1992; U.S. Patent 4,849,484, to Heard, issued July 18, 1989; U.S. Patent 4,635,206, to Farrar et al., issued May 30, 1989; U.S. Patent 4,628,078 to Glover et al. issued December 9, 1986; U.S. Patent 4,599,379 to Flesher et al. issued July 8, 1986; and EP 228,868, to Farrar et al., published July 15, 1987; all of which are incorporated by reference herein in their entirety.

The polymers hereof can be characterized by the general formula:  $(A)_m(B)_n(C)_p$  wherein (A) is a dialkylaminoalkyl acrylate monomer or its quaternary ammonium or acid addition salt, (B) is a dialkylaminoalkyl methacrylate monomer or its quaternary ammonium or acid addition salt, (C) is a nonionic monomer that is polymerizable with (A) or (B) having a carbon-carbon double bond, that is polymerizable

with (A) or (B). m is an integer of 0 or greater, n is an integer of 0 or greater, and p is an integer of 0 or greater, wherein either m or n, or both, must be 1 or greater.

The (C) monomer can be selected from any of the commonly used monomers. Nonlimiting examples of these monomers include ethylene, propylene, butylene, isobutylene, eicosene, maleic anhydride, acrylamide, methacrylamide, maleic acid, acrolein, cyclohexene, ethyl vinyl ether, and methyl vinyl ether. In the cationic polymers of the present invention, (C) is preferably acrylamide. The alkyl portions of the (A) and (B) monomers are short chain length alkyls such as C<sub>1</sub>-C<sub>8</sub>, preferably C<sub>1</sub>-C<sub>5</sub>, more preferably C<sub>1</sub>-C<sub>3</sub>, most preferably C<sub>1</sub>-C<sub>2</sub>. When quaternized, the polymers are preferably quaternized with short chain alkyls, i.e., C<sub>1</sub>-C<sub>8</sub>, preferably C<sub>1</sub>-C<sub>5</sub>, more preferably C<sub>1</sub>-C<sub>3</sub>, most preferably C<sub>1</sub>-C<sub>2</sub>. The acid addition salts refer to the (A) and (B) monomers of the polymers having protonated amino groups. Acid addition salts can be preformed through the use of halogen (e.g. chloride), acetic, phosphoric, nitric, citric, or other acids.

These (A)<sub>m</sub>(B)<sub>n</sub>(C)<sub>p</sub> polymers also contain a crosslinking agent, which is typically a material containing two or more unsaturated functional groups. The crosslinking agent is reacted with the monomer units of the polymer and is incorporated into the polymer, forming either links or covalent bonds between two or more individual polymer chains or between two or more sections of the same polymer chain. Nonlimiting examples of suitable crosslinking agents include those selected from the group consisting of methylenebisacrylamides, diacrylates, dimethacrylates, di-vinyl aryl (e.g. di-vinyl phenyl ring) compounds, polyalkenyl polyethers of polyhydric alcohols, allyl acrylates, vinyloxyalkylacrylates, and polyfunctional vinylidenes. Specific examples of crosslinking agents useful herein include those selected from the group consisting of methylenebisacrylamide, ethylene glycol, propylene glycol, butylene glycol, di-(meth)acrylate, di-(meth)acrylamide, cyanomethylacrylate, vinyloxyethylacrylate, vinyloxyethylmethacrylate, allyl pentaerythritol, trimethylolpropane diallylether, allyl sucrose, butadiene, isoprene, 1,4 di-ethylene benzene, divinyl naphthalene, ethyl vinyl ether, methyl vinyl ether, and allyl acrylate. Other crosslinkers include formaldehyde and glyoxal.

Preferred for use herein as a crosslinking agent is methylenebisacrylamide.

Widely varying amounts of the crosslinking agent can be employed depending upon the properties desired in the final polymer. e.g. viscosifying effect. The crosslinking agent will typically comprise from about 1 ppm to about 10,000 ppm, preferably from about 5 ppm to about 750 ppm, more preferably from about 25 ppm to about 500 ppm, even more preferably from about 100 ppm to about 500 ppm, and most preferably from about 250 ppm to about 500 ppm of the total weight of the polymer on a weight/weight basis.

The intrinsic viscosity of the crosslinked polymer can be measured to characterize the polymer. This intrinsic viscosity is distinct from the viscosity measurement used to characterize the total hair care composition of the present invention. The intrinsic viscosity of the crosslinked polymer can be measured in one molar sodium chloride solution at 25°C, is generally above 6, preferably from about 8 to 14. The molecular weight (weight average) of the crosslinked polymers hereof is high, and is believed to typically be between about 1 million and about 30 million. The specific molecular weight is not critical and lower or higher weight average molecular weights can be used. The crosslinked polymers are preferably characterized in a 1.0% solution of the polymer in deionized water to have a viscosity, at 25°C, of at least about 20,000 cP, preferably at least about 30,000 cP, when measured at 20 RPM by a Brookfield RVT (Brookfield Engineering Laboratories, Inc. Stoughton, MA, USA).

These cationic polymers can be made by polymerization of an aqueous solution containing from about 20% to about 60%, generally from about 25% to about 40%, by weight monomer, in the presence of an initiator (usually redox or thermal) until the polymerization terminates. The crosslinking agent can also be added to the solution of the monomers to be polymerized, to incorporate it into the polymer. In the polymerization reactions, the temperature generally starts between about 0° and 95°C. The polymerization can be conducted by forming a reverse phase dispersion of an aqueous phase of the monomers (and also any additional crosslinking agents) into a nonaqueous liquid, e.g. mineral oil, lanolin, isododecane, oleyl alcohol, and other volatile and nonvolatile esters, ethers, and alcohols, and the like.

All percentages describing the polymer in this section of the description herein are molar, unless otherwise specified. When the polymer contains (C) monomer, the molar proportion of C, based on the total molar amount of A, B, and C, can be from 0% to about 99%. The 5 molar proportions of (A) and (B) can each be from 0% to 100%. When acrylamide is used as the "C" monomer, it will preferably be used at a level of from about 20% to about 99%, more preferably from about 50% to about 90%.

Where monomer A and B are both present, the ratio of monomer 10 A:monomer B in the final polymer, on a molar basis, is preferably about 99:5 to about 15:85, more preferably from about 80:20 to about 20:80.

Alternatively, in another class of polymers, the ratio is from about 5:95 to about 50:50, preferably from about 5:95 to about 25:75.

In another alternative class the ratio A:B is from about 50:50 to 15 about 85:15. Preferably the ratio A:B is from about 60:40 to about 85:15, most preferably from about 75:25 to about 85:15.

Most preferred in the present invention is where neither monomer A nor monomer C is present. Cationic polymers useful herein that are especially preferred are those conforming to the general structure 20 (A)<sub>m</sub>(B)<sub>n</sub>(C)<sub>p</sub> wherein m is zero, (B) is methyl quaternized dimethylaminoethyl methacrylate, p is zero, and the crosslinking agent is methylenebisacrylamide. An example of such a homopolymer is polyquaternium 37. The homopolymer can be used alone or in a suitable carrier such as mineral oil or propylene glycol dicaprylate/dicaprate. This homopolymer is commercially available as a mineral oil dispersion also containing PPG-1 trideceth-6 as a dispersing aid, from Allied Colloids Ltd. (Norfolk, VA) under the trademark Salcare® SC95 or as a dispersion in propylene glycol dicaprylate/dicaprate also containing PPG-1 trideceth-6 as a dispersing aid, from Allied Colloids 25 Ltd. (Norfolk, VA) under the trademark Salcare® SC96.

#### Salt

The compositions of the present invention comprise from about 0.1% to about 10%, more preferably from about 0.2% to about 5%, and most 35 preferably from about 0.5% to about 3% of a salt. Without being limited by theory, the salt is believed to provide a viscosity reduction effect on the polymer in the polar solvent of the present invention.

The salt of the present invention comprises a mixture of monomeric cations and anions. The salt of the present invention comprises monomeric ions of the type which are products of acid-base reactions. The salt can be incorporated into the hair care compositions, for example, by addition of soluble salts, or by addition of mixtures of acids and bases, or by a combination thereof. It is a necessary aspect of the invention that both anions and cations of the salt be included in the composition.

Suitable cations for use include, for example, alkali metals, such as lithium, sodium, and potassium, alkaline-earth metals, such as magnesium, calcium, and strontium, and transition metals such as aluminum, copper, zinc, iron and the like. Preferred of the divalent cations is magnesium. Preferred monovalent metal ions are lithium, sodium, and potassium, particularly sodium and potassium. Suitable means of addition to the compositions hereof include, for example, addition as bases, e.g., hydroxides, sodium hydroxide and potassium hydroxide, and such as salts that are soluble in the polar solvent, e.g. salts of monomeric anions such as those described below.

Other suitable cations include organic ions, such as quaternary ammonium ions and cationic amines, such as ammonium mono-, di-, and tri-ethanolamines, triethylamine, morpholine, aminomethylpropanol (AMP), aminoethylpropanediol, etc. Ammonium and the amines are preferably provided in the forms of salts, such as hydrochloride salts.

Anions that can be used include halogen ions, such as chloride, fluoride, bromide, and iodide, sulfate, ethyl sulfate, methyl sulfate, cyclohexyl sulfamate, thiosulfate, toluene sulfonate, xylene sulfonate, citrate, nitrate, bicarbonate, adipate, succinate, saccharinate, benzoate, lactate, borate, isethionate, tartrate, acetate, ethylene diamine tetra acetate and other anions that can exist in dissociated form in the hair care composition. The anions can be added to the compositions hereof, for example, in the form of acids or salts which are at least partially soluble in the liquid vehicle. Preferred anions include acetate, ethylene diamine tetra acetate, citrate, nitrate, chloride, phosphate and sulfate, etc. More preferred is ethylene diamine tetra acetate.

Preferred salts of the compositions of the present invention include sodium acetate, potassium acetate, ammonium acetate, sodium citrate, potassium citrate, ammonium citrate, sodium nitrate, potassium nitrate, ammonium nitrate, sodium phosphate, potassium phosphate, ammonium

phosphate, sodium chloride, potassium chloride, ammonium chloride, sodium sulfate, potassium sulfate, ammonium sulfate, sodium ethylene diamine tetra acetic acid, disodium ethylene diamine tetra acetic acid and trisodium ethylene diamine tetra acetic acid, tetra sodium ethylene diamine 5 tetra acetate and mixtures thereof. Most preferred is disodium ethylene diamine tetra acetic acid.

Ratio of Crosslinked Polymeric Conditioning Agent to Salt

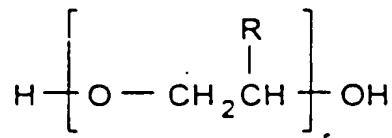
The compositions of the present invention must comprise a critical weight ratio of cationic crosslinked polymeric conditioning agent to salt of 10 from about 1:25 to about 25:1, preferably from about 1:10 to about 15:1, and more preferably from about 1:1 to about 10:1.

Polyalkylene Glycol

The compositions of the present invention comprise at least one polyalkylene glycol. The polyalkylene glycol typically comprises from about 15 0.0001% to about 0.05%, preferably from about 0.0005% to about 0.03%, and more preferably from about 0.001% to about 0.02%, by weight of the total composition.

The polyalkylene glycols useful herein are those corresponding to the following formula:

20



In the preceding formula R is selected from the group consisting of H, CH<sub>3</sub>, and mixtures thereof, preferably R is H. When R is H, the polyalkylene glycol is a polyethylene glycol, i.e. the polyalkylene glycol is composed of repeating units that are derived from ethylene glycol or ethylene oxide. When R is CH<sub>3</sub>, the polyalkylene glycol is a polypropylene glycol, i.e. the polypropylene glycol is composed of repeating units that are derived from propylene glycol or propylene oxide. In the preceding formula r is an integer 25 from about 2000 to about 25,000, preferably from about 2000 to about 15000, and more preferably about 2000 to about 7000. Without being limited by theory, it is believed that the polyethylene glycol helps reduce the hydrodynamic drag of the solution and the dip tube of a spray bottle 30 resulting in improved spray characteristics such as a well-defined, uniform spray volume.

35

Polar Solvent

The leave-on hair care compositions of the present invention also comprise a polar solvent as a liquid vehicle for the crosslinked polymeric conditioning agent. A polar solvent is any solvent material with a dielectric constant at 25°C greater than about 5.0, preferably greater than about 7.5 and more preferably greater than about 10.0. The polar solvent of the present invention comprises one or more polar solvents that are present in the hair care compositions at a level of from about 60% to about 99.7999%, preferably from about 85% to about 98%, more preferably from about 90% to about 95% of the total composition.

The polar solvents essential to the present compositions are selected from the group consisting of water, C<sub>2</sub>-C<sub>3</sub> monohydric alkanols, and mixtures thereof. If present, C<sub>3</sub> alkanols, such as isopropanol, should be used at levels no greater than about 15% by weight of the composition, preferably no greater than about 12%, more preferably no greater than about 10%. High levels of C<sub>3</sub> monohydric alcohols are undesirable in the present compositions due to potential odor issues they can create. Preferred polar solvent phases contain water, ethanol, or mixtures thereof.

Where water and alcohol mixtures are used, for instance, water-ethanol or water-isopropanol-ethanol, the water content of the compositions is generally in the range of from about 0.5% to about 99%, by weight of the total composition. In such mixtures, the alcohol solvents are generally present in the range of from 0.5% to about 99%, by weight of the total composition.

25 Viscosity

The composition of the present invention mixture comprising a viscosity, at 25°C, of from about 10 to about 500 cP, preferably from about 50 cP to about 200 cP, and more preferably from about 100 cP to about 200 cP. Viscosity is determined using a Brookfield Digital Viscometer Model DV-II, Spindel #41, at 25°C, at 10 RPM for three minutes.

Optional Ingredients

The hair care compositions of the present invention can be formulated in a variety of product types which have low viscosity, including tonics, sprays and mousses. Therefore the present compositions can contain a wide variety of optional ingredients, including among them any of the types of ingredients known in the art for use in hair care products, especially hair spray and hair tonic compositions. These ingredients

include, but are not limited to, insoluble silicone fluids, gums and resins, volatile silicone solvents, non-solubilized particulates, surfactants, dispersing aids, styling resins, propellants and others.

Silicone Conditioning Agents

5        The compositions hereof can optionally include nonvolatile soluble or insoluble silicone conditioning agents or volatile silicone conditioning agents. By soluble what is meant is that the silicone conditioning agent is miscible with the aqueous carrier of the composition so as to form part of the same phase. By insoluble what is meant is that the silicone forms a separate, 10 discontinuous phase from the aqueous carrier, such as in the form of an emulsion or a suspension of droplets of the silicone. The term "nonvolatile" as used herein shall mean that the silicone has a boiling point of at least about 260°C, preferably at least about 275°C, more preferably at least about 15 300°C. Such materials exhibit very low or no significant vapor pressure at ambient conditions. The term volatile shall mean that the silicone has a boiling point of from about 99°C to about 260°C.

20      The silicone hair conditioning agent will be used in the leave-on hair care compositions of the present invention at levels of from about .05% to about 10% by weight of the composition, preferably from about 0.1% to about 3%, more preferably from about 0.5% to about 5%, most preferably from about 0.5% to about 3%.

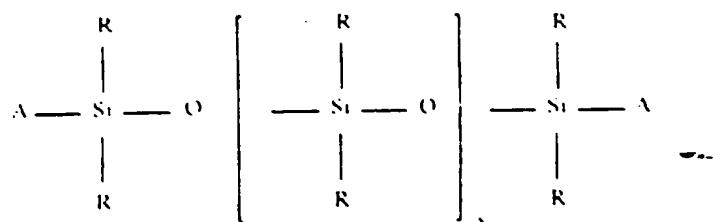
25      Soluble silicones include silicone copolyols, such as dimethicone copolyols, e.g. polyether siloxane-modified polymers, such as polypropylene oxide, polyethylene oxide modified polydimethylsiloxane, wherein the level of ethylene and/or propylene oxide sufficient to allow solubility in the composition.

30      Preferred, however, are insoluble silicones. The insoluble silicone hair conditioning agent for use herein will preferably have viscosity of from about 1,000 to about 2,000,000 centistokes at 25°C, more preferably from about 10,000 to about 1,800,000, even more preferably from about 100,000 to about 1,500,000. The viscosity can be measured by means of a glass capillary viscometer as set forth in Dow Corning Corporate Test Method CTM0004, July 20, 1970.

35      Suitable insoluble, nonvolatile silicone fluids include polyalkyl siloxanes, polyaryl siloxanes, polyalkylaryl siloxanes, polyether siloxane copolymers, and mixtures thereof. Other insoluble, nonvolatile silicone fluids having hair conditioning properties can also be used. The term

"silicone fluid" shall mean flowable silicone materials having a viscosity of less than 1,000,000 centistokes at 25°C. Generally, the viscosity of the fluid will be between about 5 and 1,000,000 centistokes at 25°C, preferably between about 10 and about 300,000.

5      Silicone fluids hereof also include polyalkyl or polyaryl siloxanes with the following structure:



10     wherein R is alkyl or aryl, and x is an integer from about 7 to about 8,000 may be used. "A" represents groups which block the ends of the silicone chains.

15     The alkyl or aryl groups substituted on the siloxane chain (R) or at the ends of the siloxane chains (A) may have any structure as long as the resulting silicones remain fluid at room temperature, are hydrophobic, are neither irritating, toxic nor otherwise harmful when applied to the hair, are compatible with the other components of the composition, are chemically stable under normal use and storage conditions, and are capable of being deposited on and of conditioning hair.

20     Suitable A groups include methyl, methoxy, ethoxy, propoxy, and aryloxy. The two R groups on the silicone atom may represent the same group or different groups. Preferably, the two R groups represent the same group. Suitable R groups include methyl, ethyl, propyl, phenyl, methylphenyl and phenylmethyl. The preferred silicones are polydimethyl siloxane, polydiethylsiloxane, and polymethylphenylsiloxane. Polydimethylsiloxane is especially preferred.

25     The nonvolatile polyalkylsiloxane fluids that may be used include, for example, polydimethylsiloxanes. These siloxanes are available, for example, from the General Electric Company in their Viscasil R® and SF96® series, and from Dow Corning in their Dow Corning 200® series.

30     The polyalkylaryl siloxane fluids that may be used, also include, for example, polymethylphenylsiloxanes. These siloxanes are available, for example, from the General Electric Company as SF1075® methyl phenyl fluid or from Dow Corning as 556 Cosmetic Grade Fluid®.

Especially preferred, for enhancing the shine characteristics of hair, are highly arylated silicones, such as highly phenylated polyethyl silicone having refractive indices of about 1.46 or higher, especially about 1.52 or higher. When these high refractive index silicones are 5 used, they should be mixed with a spreading agent, such as a surfactant or a silicone resin, as described below to decrease the surface tension and enhance the film forming ability of the material.

The polyether siloxane copolymers that may be used include, for example, a polypropylene oxide modified polydimethylsiloxane (e.g., 10 Dow Corning DC-1248®) although ethylene oxide or mixtures of ethylene oxide and propylene oxide may also be used. The ethylene oxide and polypropylene oxide level should be sufficiently low to prevent solubility in the composition hereof.

References disclosing suitable silicone fluids include U.S. Patent 15 2,826,551, Geen; U.S. Patent 3,964,500, Drakoff, issued June 22, 1976; U.S. Patent 4,364,837, Pader; and British Patent 849,433, Woolston. All of these patents are incorporated herein by reference:

Another silicone hair conditioning material that can be especially useful in the silicone conditioning agents is insoluble silicone gum. The 20 term "silicone gum", as used herein, means polyorganosiloxane materials having a viscosity at 25°C of greater than or equal to 1,000,000 centistokes. Silicone gums are described by Petrarch and others including U.S. Patent 4,152,416, Spitzer et al., issued May 1, 1979 and Noll, Walter, Chemistry and Technology of Silicones, New York: Academic Press 1968. The "silicone gums" will typically have a mass 25 molecular weight in excess of about 200,000, generally between about 200,000 and about 1,000,000. Specific examples include polydimethylsiloxane, (polydimethylsiloxane) (methylvinylsiloxane) copolymer, poly(dimethylsiloxane) (diphenyl siloxane)(methylvinylsiloxane) copolymer and mixtures thereof.

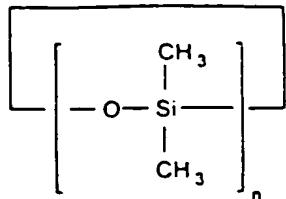
Preferably the silicone hair conditioning agent comprises a mixture of a polydimethylsiloxane gum, having a viscosity greater than about 1,000,000 centistokes and polydimethylsiloxane fluid having a viscosity of from about 10 centistokes to about 100,000 centistokes, 35 wherein the ratio of gum to fluid is from about 30:70 to about 70:30, preferably from about 40:60 to about 60:40.

The polydimethylsiloxane gum/polydimethylsiloxane fluid can be used alone or in a suitable carrier such as polysorbate 80. The combination of gum, fluid and polysorbate 80 is commercially available as CM 2233® from GE Silicones.

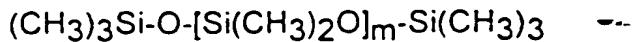
5 An optional ingredient that can be included in the silicone conditioning agent is silicone resin. Silicone resins are highly crosslinked polymeric siloxane systems. The crosslinking is introduced through the incorporation of trifunctional and tetrafunctional silanes with monofunctional or difunctional, or both, silanes during manufacture of the  
10 silicone resin. As is well understood in the art, the degree of crosslinking that is required in order to result in a silicone resin will vary according to the specific silane units incorporated into the silicone resin. In general, silicone materials which have a sufficient level of trifunctional and tetrafunctional siloxane monomer units (and hence, a sufficient level of  
15 crosslinking) such that they dry down to a rigid, or hard, film are considered to be silicone resins. The ratio of oxygen atoms to silicon atoms is indicative of the level of crosslinking in a particular silicone material. Silicone materials which have at least about 1.1 oxygen atoms per silicon atom will generally be silicone resins herein. Preferably, the  
20 ratio of oxygen:silicon atoms is at least about 1.2:1.0. Silanes used in the manufacture of silicone resins include monomethyl-, dimethyl-, trimethyl-, monophenyl-, diphenyl-, methylphenyl-, monovinyl-, and methylvinyl-chlorosilanes, and tetrachlorosilane, with the methyl-substituted silanes being most commonly utilized. Preferred resins are  
25 offered by General Electric as GE SS4230® and SS4267®. Commercially available silicone resins will generally be supplied in a dissolved form in a low viscosity volatile or nonvolatile silicone fluid. The silicone resins for use herein should be supplied and incorporated into the present compositions in such dissolved form, as will be readily  
30 apparent to those skilled in the art.

Another optional silicone conditioning agent is volatile silicone solvent. The volatile silicone solvent, if present, is at a level of from about 0.01% to about 10%, preferably from about 0.05% to about 5%, by weight, of the composition. The volatile silicone allows for easier and  
35 more even dispersion of silicone gums and resins in hair care compositions. The silicones may be either cyclic or linear polydimethyl siloxanes. The number of silicon atoms in the cyclic silicones is from

about 3 to about 7, most preferably 4 or 5. The general formula for the cyclic silicones is:



wherein n=3-7. Linear polydimethyl siloxanes useful in the present invention generally contain from about 3 to about 9 silicon atoms and have the general formula:



wherein m=1-7.

Volatile silicone solvents of the above described types are widely available, e.g. from Dow Corning as 344, 345 and 200 Fluids®; Union Carbide as Silicone 7202 and 7158®; and Stauffer Chemical as SWS-03314®. The preferred volatile silicone solvent of the present invention is cyclomethicone available from General Electric Silicones. If present, it is present at from about 0.05% to about 5.0%.

Background material on silicones including sections discussing silicone fluids, gums, and resins, as well as manufacture of silicones, can be found in Encyclopedia of Polymer Science and Engineering, Volume 15, Second Edition, pp 204-308. John Wiley & Sons, Inc., 1989, incorporated herein by reference.

#### Hair Styling Resins

Another optional ingredient of the hair care compositions of the present invention is hair styling resins. Any hair hold polymer soluble or dispersible in the polar solvent phase of the present invention may be used. Suitable types of polymers include anionic, non-ionic, amphoteric and cationic polymer materials. Specific polymers include polyvinylpyrrolidone (PVP), copolymers of PVP and methylmethacrylate, copolymers of PVP and vinylacetate (VA), polyvinyl alcohol (PVA), copolymers of PVA and crotonic acid, copolymers of PVA and maleic anhydride, hydroxypropyl cellulose, hydroxypropyl guar gum, sodium polystyrene sulfonate, PVP/ethylmethacrylate/methacrylic acid terpolymer, vinyl acetate/crotonic acid/vinyl neodecanoate copolymer, octylacrylamide/acrylates copolymer, monoethyl ester of poly(methyl vinyl ether-maleic acid), and

octylacrylamide/acrylate/butylaminoethyl methacrylate copolymers, acrylic acid/t-butyl acrylate copolymers, dimethylaminoethyl methacrylate/isobutyl methacrylate/2-ethylhexyl-methacrylate terpolymers, t-butylacrylate/acrylic acid copolymers, and silicone grafted terpolymers, e.g. t-butylacrylate/acrylic acid/PDMS and mixtures thereof. PVP and PVP copolymers with other monomers are preferred. The most preferred resins for use in the present hair care compositions are copolymers of polyvinyl pyrrolidone and vinyl acetate (PVP/VA).

Additional hair styling polymers which can be optionally added to the compositions of the present invention include silicone-containing hair styling resins. The silicone-containing polymers are characterized by polysiloxane moieties covalently bonded to and pendant from a polymeric carbon-based backbone. The backbone is preferably a carbon chain derived from polymerization of ethylenically unsaturated monomers, but can also be cellulosic chains or other carbohydrate-derived polymeric chains to which polysiloxane moieties are pendant. The backbone can also include ether groups, ester groups, amide groups, urethane groups and the like. The polysiloxane moieties can be substituted on the polymer or can be made by co-polymerization of polysiloxane-containing polymerizable monomers (e.g. ethylenically unsaturated monomers, ethers, and/or epoxides) with non-polysiloxane-containing polymerizable monomers.

The preferred silicone-containing polymers comprise an organic backbone preferably a carbon backbone derived from ethylenically unsaturated monomers, such as a vinyl polymeric backbone, and a polysiloxane macromer (especially preferred are polydialkylsiloxane, most preferably polydimethylsiloxane) grafted to the backbone.

Silicone-containing polymers disclosed in EPO Application 90307528.1, published as EPO Application 0 408 311 A2 on January 11, 1991, Hayama, et al., U.S. Patent 5,061,481, issued October 29, 1991, Suzuki et al., U.S. Patent 5,106,609, Bolich et al., issued April 21, 1992, U.S. Patent 5,100,658, Bolich et al., issued March 31, 1992, U.S. Patent 5,100,657, Ansher-Jackson, et al., issued March 31, 1992, U.S. Patent 5,104,646, Bolich et al., issued April 14, 1992, U.S. Serial No. 07/758,319, Bolich et al., filed August 27, 1991, and U.S. Serial No. 07/758,320, Torgerson et al., filed August 27, 1991, all of which are incorporated by reference herein.

When used, the hair styling resins are used at a level of from about 0.25% to about 20%, preferably from about 0.5% to about 10% of the composition.

#### Other Ingredients

5       The compositions of the present invention can comprise a wide range of additional components suitable for rendering such compositions more cosmetically or aesthetically acceptable or to provide them with additional usage benefits. The CTFA Cosmetic Ingredient Handbook, Second Edition, 1992, which is incorporated by reference herein in its entirety, describes a

10      wide variety of nonlimiting cosmetic ingredients commonly used in the hair care industry. These additional ingredients include: other conditioning agents; detergents surfactants, such as anionic, nonionic, amphoteric, and zwitterionic surfactants; suspending agents, such as xanthan gum, guar gum, hydroxyethyl cellulose, methyl cellulose, hydroxyethylcellulose, starch

15      and starch derivatives; preservatives such as benzyl alcohol, methyl paraben, propyl paraben and imidazolidinyl urea; pH adjusting agents; coloring agents, such as any of the FD&C or D&C dyes; hair oxidizing (bleaching) agents, such as hydrogen peroxide, perborate and persulfate salts; hair reducing agents, such as the thioglycolates; perfumes; polymer

20      plasticizing agents, such as glycerin, dibutyl adipate, butyl stearate, and propylene glycol; vitamins and derivatives thereof, such as panthenol and other derivatives of pantothenic acid, pantothenic ethers; vitamin penetration aids, such as polyethylene glycol or polypropylene glycol having from 3 to about 12 ethylene glycol or propylene glycol units. Such

25      optional ingredients generally are used individually at levels from about 0.01% to about 10.0%, preferably from about 0.05% to about 5.0% of the composition.

#### METHOD OF USE

30      The hair care compositions of the present invention are used in conventional ways to provide the conditioning and damage protection benefits of the present invention. Such method of use depends upon the type of composition employed but generally involves application of a safe and effective amount of the product to the hair and allowed to remain on the hair. By "effective amount" is means an amount sufficient enough to provide a hair conditioning benefit. In general, from about 1g to about 50g is applied to the hair on the scalp. The composition is distributed throughout the hair by a spray pump as described below. Preferably, the composition is applied

35

to wet or damp hair prior to drying of the hair. After such compositions are applied to the hair, the hair is dried and styled in accordance with the desires of the user and in the usual ways of the user. Alternately, the composition is applied to dry hair, and the hair is then combed or styled in  
5 accordance with the desires of the user.

#### Dispensing Device

The dispensing devices of the present invention are preferably, but not limited to, non-aerosol mechanical spray pumps comprising a container (bottle) and a pump mechanism which securely screws or snaps onto the  
10 container, as described below.

The bottle comprises a vessel for containing the composition to be dispensed.

The pump mechanism comprises a pump chamber of substantially fixed volume, having an opening at the inner end thereof. Within the pump  
15 chamber is located a pump stem having a piston on the end thereof disposed for reciprocal motion in the pump chamber. The pump stem has a passageway therethrough with a dispensing outlet at the outer end of the passageway and an axial inlet port located inwardly thereof.

The pump mechanism also comprises a rigid valve member having  
20 an outer, an inner, and an intermediate part. The outer part terminates in a flattened top portion and a sealing surface adjacent to the flattened top portion, which seals against the axial inlet port. The outer part of the rigid valve is of a first cross section. The inner part of the rigid valve member is of a larger cross section than the outer part, and of a length corresponding  
25 to the range of movement of the piston. The intermediate portion of the rigid valve forms a generally conically tapered recess with a wide edge and a narrow end between the inner and outer parts of the rigid valve member. The recess is tapered at an acute angle with respect to the axis of the inner part. A passage leads from the axial inner end of the inner part to the  
30 tapered recess. The intermediate portion opens in the vicinity of its outer end permitting communication between the recess and the area above the inner portion. A ball having a diameter which is less than the diameter of the wide edge of the tapered recess but greater than the diameter of the narrow end, is snapped into the tapered recess to thereby form a check  
35 valve, the valve member thereby forming an inlet valve to the pump chamber. The pump mechanism further comprises a throat at the opening at the inner end of the pump chamber. As the pump is operated by depres-

sing the pump stem, the radially outer portion of the inner part of the valve member cooperates with the throat to form a means for sealing the inner end of the pump chamber with a surface to surface seal at the throat to prevent any flow from the pump chamber through the throat when the pump 5 is dispensing.

The pump mechanism further comprises a dip tube for supplying emulsion in a bottle to the throat, and a spring biasing the valve member outwardly so that the first end portion thereof closes off the inlet port, thereby also biasing the pump stem outwardly.

10 The pump mechanism also comprises a cross-sectional area closed off at the inlet port being smaller than the cross-sectional area of the second end portion of the valve member at the point where it is sealingly guided.

15 The pump mechanism also comprises an orifice cup defining an orifice through which the material to be dispensed is ejected as an atomized spray as the pump is operated. The orifice cup has an inner diameter in the range from about 0.010 inches (0.0254 cm) to about 0.016 inches (0.0406 cm) and an inner length in the range from about 0.020 inches (0.0508 cm) to about 0.060 inches (0.152 cm). A preferred combination of orifice diameter and length is 0.013 inches (0.0330 cm) and 0.040 inches (0.102 cm), 20 respectively. Molded in the backside of the orifice cup and leading tangentially or radially to the orifice is an array of at least three channels. Preferred embodiments of the present invention comprise four tangentially-oriented channels.

25 The container and pump mechanism are made of materials well known to those of skill in the art and include, but not limited to: polyethylene; polypropylene; polyethyleneterephthalate; blends of polyethylene, vinyl acetate, and rubber elastomer (e.g., Tri-Blend 801 available from American Gasket, Schiller Park, IL); Acetal (available as Celcon<sup>R</sup> from Hoechst-Celanese Corp., Chatham, NJ); Buna P Rubber (available from American Gasket, Schiller Park, IL); and mixtures thereof. Other materials can include stainless steel.

30 The compositions of the present invention provide a reduced number of finger pumps to prime the pump for dispensing product and thus provide greater ease of dispensing product.

35 A variety of commercially available dispensing devices can be employed as part of the present invention. These dispensing devices include, but are not limited to, those described in: U.S. Patent No.

4,895,279, to Shultz, issued January 23, 1990; U.S. Patent No. 4,735,347, to Schultz and Meshberg, issued April 5, 1988; and U.S. Patent No. 4,274,560, to Cater, issued June 23, 1981; the disclosures of all these patents being incorporated herein by reference in their entirety. Such 5 dispensing devices are commercially available from Emson Research, Inc., Bridgeport, CT.

### EXAMPLES

The following examples illustrate the present invention. It will be appreciated that other modifications of the present invention within the skill 10 of those in the hair care formulation art can be undertaken without departing from the spirit and scope of this invention.

All parts, percentages, and ratios herein are by weight unless otherwise specified. Some components are obtained from suppliers as dilute solutions. The levels given reflect the weight percent of the active 15 material, unless otherwise specified.

#### Non-aerosol Hair Sprays

Non-aerosol hair conditioning spray compositions of the present invention are prepared as follows:

	<u>Component (wt%)</u>	<u>Example No.</u>				
		<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
20	Salcare® SC96 (1)	1.00	0.00	0.70	2.00	1.00
	Salcare® SC95 (2)	0.00	1.00	0.00	0.00	0.00
	Silicone Emulsion (3)	0.00	1.00	1.00	2.00	0.60
	PVP/VA Copolymer (4)	0.00	1.00	0.00	2.00	1.00
25	Polyethylene Glycol 4	0.50	0.50	0.00	0.50	0.45
	Polyethylene Glycol 5000	0.005	0.01	0.00	0.10	0.01
	Disodium EDTA	1.00	0.15	0.15	0.75	0.15
	Preservative	0.35	0.35	0.35	0.35	0.35
	Fragrance	1.00	1.00	1.00	1.00	0.05
30	Ethanol	0.00	70.00	0.00	0.00	0.00
	Panthenol	0.05	0.02	0.00	0.02	0.05
	Crotein Q (5)	0.00	0.00	0.02	0.00	0.01
	Panthenyl-Ethyl-Ether	0.02	0.25	0.00	0.25	0.01
	OMC (6)	0.00	0.00	0.00	0.00	0.01
35	Silk Amino Acids (7)	0.00	0.02	0.00	0.00	0.01
	Water	97.00	24.99	96.80	91.90	96.30

1 Polyquaternium 37 (and) Propylene Glycol Dicaprylate/Dicaprante (and) PPG-1 Trideceth 6, commercially available from Allied Colloids Ltd., (Norfolk, VA, USA).

2 Polyquaternium 37 (and) Mineral Oil (and) PPG-1 Trideceth 6, 5 commercially available from Allied Colloids Ltd., (Norfolk, VA, USA).

3 Premix of polydimethylsiloxane gum/polydimethylsiloxane fluid (40:60 ratio) from GE Silicones and up to 30% polysorbate 80.

4 PVP/VA (70/30) available from ISP

5 Hydrolyzed Animal Protein available from Croda, Inc.

10 6 Octylmethoxy cinnamate, available from Givaudan-Roure, Inc.

7 Crosilk Liquid, available from Croda, Inc.

These products are prepared by dissolving the Salcare® SC96 (1) in the water and/or ethanol and mixing for several minutes until all of the premix is dissolved. The remaining ingredients are then added. Fragrance 15 is added last. All ingredients are added under mixing conditions. The product can be packaged in conventional nonaerosol pump spray containers and compressed air pump spray aerosol containers.

These compositions are found to have a viscosity, at 25°C, between 10 cP and 500 cP.

20 These compositions provide are useful as leave-on hair care products, which provide conditioning and damage protection benefits.

Example No.

	<u>Component (wt%)</u>	<u>6</u>	<u>7</u>	<u>8</u>
	Salcare® SC96 (1)	0.70	0.5	0.05
25	Ethanol	79.00	79.0	86.40
	Silicone Emulsion (2)	0.50	0.00	1.00
	Diisobutyl Adipate	0.70	0.00	0.00
	Potassium Hydroxide Solution (45% conc)	1.00	1.00	1.00
30	Gantrez ES225® (3)	8.00	8.00	8.00
	Disodium EDTA	0.15	0.15	0.15
	Perfume	0.20	0.20	0.20
	Water	9.75	11.15	3.20
35	1 Polyquaternium 37 (and) Propylene Glycol Dicaprylate/Dicaprante (and) PPG-1 Trideceth 6, commercially available from Allied Colloids Ltd., (Norfolk, VA, USA).			

2. Premix of polydimethylsiloxane gum/polydimethylsiloxane fluid (40:60 ratio) from GE Silicones and up to 30% polysorbate 80.

3. Poly (methylvinyl ether / maleic acid) monoethyl ester, 50% solids in ethanol. Organic resin, commercially available from ISP.

5 These products are prepared by dissolving the Salcare® SC96 (1) in the ethanol and mixing for several minutes until all of the Salcare is dissolved. Diisobutyl Adipate is then added, if applicable. Potassium hydroxide is then added. Water and remaining ingredients are added. Fragrance is added last. All ingredients are added under mixing conditions.

10 The product can be packaged in conventional nonaerosol pump spray containers and compressed air pump spray aerosol containers.

These compositions are found to have a viscosity, at 25°C, between 10 cP and 500 cP.

15 These compositions provide are useful as leave-on hair care products, which provide conditioning and damage protection benefits.

## WHAT IS CLAIMED IS:

1. An atomizable leave-on hair care composition characterized in that it comprises:

5 (i) from 0.1% to 10%, preferably from 0.2% to 5%, more preferably from 0.5% to 3%, by weight, of a cationic crosslinked polymeric conditioning agent comprising the monomer units  $(A)_m (B)_n (C)_p$  and a crosslinking agent wherein:

(A) is a dialkylaminoalkyl acrylate monomer or a quaternary ammonium or acid addition salt thereof;

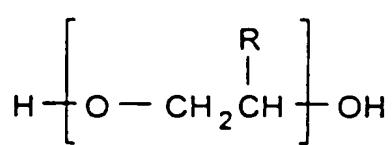
10 (B) is a dialkylaminoalkyl methacrylate monomer or a quaternary ammonium or acid addition salt thereof;

(C) is a nonionic monomer polymerizable with (A) or (B);

m, n, and p are independently zero or greater, but at least one of m or n is one or greater, preferably n is greater than or equal to 1 and m and p are equal to 0;

15 (ii) from 0.1% to 10%, preferably from 0.2% to 5%, more preferably from 0.5% to 3%, by weight, of a salt : and

(iii). from 0.0001% to 0.05%, preferably from 0.0005% to 0.03%, more preferably from 0.001% to 0.02% of at least one polyalkylene glycol corresponding to the structure



25 wherein R is H or  $\text{CH}_3$  and r is an integer from 2000 to 25,000, preferably from 2000 to 15000, more preferably from 2000 to 7000;

(d) from 60% to 99.7999%, preferably from 85% to 98%, more preferably from 90% to 95%, by weight, of a polar solvent;

wherein the weight ratio of said cationic crosslinked polymeric conditioning agent to said salt is from 1:25 to 25:1, preferably from 1:10 to 15:1, more preferably from 1:1 to 10:1; and

30 wherein the viscosity of the composition is from 10 cP to 500 cP, preferably from 50 cP to 200 cP, more preferably from 100 cP to 200 cPas measured using a Brookfield Viscometer, Spindel #41, at 25°C, at 10 RPM for three minutes.

2. An atomizable leave-on hair care composition according to Claim 1, wherein said crosslinking agent is selected from the group consisting of methylenebisacrylamide, ethylene glycol, propylene glycol, butylene glycol, di-(meth)acrylate, di-(meth)acrylamide, cyanomethylacrylate, vinyloxyethylacrylate, vinyloxyethylmethacrylate, allyl pentaerythritol, trimethylolpropane diallylether, allyl sucrose, butadiene, isoprene, 1,4 diethylene benzene, divinyl naphthalene, ethyl vinyl ether, methyl vinyl ether, allyl acrylate, formaldehyde, glyoxal and mixtures thereof, preferably the crosslinking agent is said methylenebisacrylamide.

10 3. An atomizable leave-on hair care composition according to either of Claims 1 and 2, wherein said (B) monomer unit is methyl quaternized dimethylaminoethyl methacrylate monomer.

4. A leave-on hair care composition according to any of Claims 1 to 3, wherein said crosslinked polymeric conditioning agent is polyquaternium 37.

5. A leave-on hair care composition according to any of Claims 1 to 4, wherein said salt comprises:

(i) a monomeric cation selected from the group consisting of lithium, sodium, potassium, magnesium, calcium, strontium, aluminum, copper, zinc, iron, monoethanciammonium, diethanolammonium, triethanolammonium, monoethylammonium, diethylammonium, triethylammonium, morpholine cation, aminomethylpropanol cation, aminoethylpropanediol cation and mixtures thereof; and

(ii) an anion selected from the group consisting of chloride, fluoride, bromide, iodide; sulfate, ethyl sulfate, methyl sulfate, cyclohexyl sulfamate, thiosulfate, toluene sulfonate, xylene sulfonate, citrate, nitrate, bicarbonate, adipate, succinate, saccharinate, benzoate, lactate, borate, isethionate, tartrate, acetate, ethylene diamine tetra acetate and mixtures thereof;

10 wherein said salt has a solubility in the polar solvent of greater than 1 percent at 25°C.

15 6. A leave-on hair care composition according to any of Claims 1 to 4, wherein said salt is selected from the group consisting of sodium acetate,

potassium acetate, ammonium acetate, sodium citrate, potassium citrate, ammonium citrate, sodium nitrate, potassium nitrate, ammonium nitrate, sodium phosphate, potassium phosphate, ammonium phosphate, sodium chloride, potassium chloride, ammonium chloride, sodium sulfate potassium sulfate, ammonium sulfate, sodium ethylene diamine tetra acetic acid, disodium ethylene diamine tetra acetic acid, trisodium ethylene diamine tetra acetic acid, tetra sodium ethylene diamine tetra acetate, and mixtures thereof; wherein said salt is fully soluble in the polar solvent, preferably the salt is said disodium ethylene diamine tetra acetic acid.

7. A leave-on hair care composition according to Claims 1 to 6 wherein said polar solvent is selected from the group consisting of water, C<sub>2</sub>-C<sub>3</sub> monohydric alkanols, and mixtures thereof.

8. A hair care composition according to Claims 1 to 7 further comprising from 0.1% to 20%, of a hair care agent selected from the group consisting of silicone conditioning agents, hair styling resins and mixtures thereof; preferably the hair care agent is selected from the group consisting of 1) a mixture of polydimethylsiloxane gum, having a viscosity greater than 1,000,000 centistokes and polydimethylsiloxane fluid having a viscosity of from 10 centistokes to 100,000 centistokes, wherein the ratio of gum to fluid is from 30:70 to 70:30; 2) a copolymer of a) polyvinyl pyrrolidone and b) vinyl acetate; and 3) mixtures thereof.

10

9. A method for conditioning human hair comprising the application of a safe and effective amount of the hair care composition according to Claims 1 to 8 to the hair of a human in need of such treatment.

# INTERNATIONAL SEARCH REPORT

Intern'l Application No  
PCT/US 97/00309

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC 6 A61K7/06

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 93 03704 A (PROCTER & GAMBLE) 4 March 1993 see the whole document -----	1-9

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

\* Special categories of cited documents :

- \*'A' document defining the general state of the art which is not considered to be of particular relevance
- \*'E' earlier document but published on or after the international filing date
- \*'L' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*'O' document referring to an oral disclosure, use, exhibition or other means
- \*'P' document published prior to the international filing date but later than the priority date claimed

\*'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*'Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

\*'A' document member of the same patent family

1

Date of the actual completion of the international search

10 June 1997

Date of mailing of the international search report

27.06.97

Name and mailing address of the ISA  
European Patent Office, P.B. 5818 Patendaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tel. 31 651 epo nl.  
Fax (+31-70) 340-2016

Authorized officer

Hillekens, G

## INTERNATIONAL SEARCH REPORT

Inten WI Application No  
PCT/US 97/00309

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9303704 A	04-03-93	AU 2502892 A BR 9206388 A CA 2115154 A CN 1071331 A CZ 9400352 A EP 0600008 A FI 940771 A HU 67488 A JP 6509807 T NO 940538 A NZ 243996 A SK 19294 A	16-03-93 27-12-94 04-03-93 28-04-93 13-07-94 08-06-94 18-02-94 28-04-95 02-11-94 14-04-94 27-06-95 07-12-94